The Semi-Industrial Fuel Cell Element of the Gaz de France

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INTRODUCTION

The studies undertaken by the laboratories of Gaz de France in the field of energy conversion have been carried out for almost four years in order to transform directly into electrical energy in a fuel cell the free energy of gases currently manufactured or distributed by this national service.

Massive quantities, relatively low prices and ease of transport of these raw materials encourage research towards perfecting industrial devices that would be simple, rugged, and inexpensive, but capable of yielding significant power. Relatively inert fuels are the usable gases: both natural gas either unreacted or catalytically steam reformed, and gas obtained by partial oxidation of gas and liquid hydrocarbons, nevertheless contain, although in small quantity, some impurities which seem to prohibit, to our knowledge, the use of sufficiently active, but sensitive catalysts which would allow functioning at moderate temperatures and in an aqueous environment. Under these conditions, it becomes necessary to counterbalance the catalytic effect by an increase in temperature and hence to operate in the presence of electrolytes made of molten salts. It seems better to make the best use of the notable advantages offered by the high temperatures providing the condition that the technological difficulties and the resulting corrosion problems can be solved.

The unavoidable heat release, provoked by any type of functioning cell, is all the more interesting to recover when the temperature of the system is high and when the dimensions of the battery are significant. The fuel cell then becomes a means of base production of electrical current which is located upstream in a complex. The other devices of this complex can use the thermal energy released by the cell.

1. PRINCIPLES OF OPERATION FOR AN INDUSTRIAL GENERATOR

Keeping these considerations in mind, the operating principle of an industrial generator can be defined in a general sense and thus serve as a constant objective towards which all investigations must be oriented.

The potential at the terminals of an elementary cell are low. For an installation to be of industrial interest it is necessary to group, in a unit well adapted to isothermal operation, the greatest possible number of elements. However, as these warm each other, they must be spaced in the most judicious way so that the regulating fluid ensures as homogeneous a temperature as possible in all parts of the enclosure; for obvious reasons air used as an oxidant can be used for this role.

Two simple geometric forms may be considered a priori for the basic cells: the plane and the cylinder. We have deliberately set our choice on the latter for the following reasons: the thermal regulation of an assembly of bundles of the exchanger type is industrially well known; the practical construction of flat and thin electrodes of large area presents more difficulties than that of tubes; the high temperature construction in the shape of a filter press creates important sealing problems and prevents any possibility of replacing an element without a complete stop in the functioning of the battery; the phenomena of diffusion or creepage of the electrolyte at the joints or in any nonactive part of the cell may be easily eliminated in tubes by cooling of the involved extremity, at a temperature slightly below that of the melting point of the fused salts; the reacting gas supply is greatly simplified where all the cells have an electrode of the same sign in a unique enclosure containing the corresponding gas; the mechanical strength of a tube made by successive layers of the anode, of the electrolyte and of the cathode, is better than that of a plane surface made under identical conditions.

The construction of a cylindrical cell battery is advantageously made through a horizontal disposition of the elements inside a heated parallelepiped shaped container of which two opposite sides form supports and to which are fixed the ends of the cells bearing the different gas distribution systems and the current collectors. In order to determine orders of magnitude, the thickness of such an installation would be close to one meter, and its length and height would be a few meters. An unlimited number of cells may be used by placing them side by side separated by a passage large enough to conduct electric current of substantial size.

Figure 1 shows the sketch of an industrial unit which would function according to the above mentioned operating principles.

2. DESCRIPTION OF THE SINGLE CELL

The conception of an element must satisfy the technological constraints which have been enumerated and give an answer to the economic problems that the development of a new technology can create.

2.1 Choice of Materials

The materials with which the electrodes are made are generally expensive and rare, and it is necessary to use them in a small quantity and to build them by simple methods relying on industrial techniques that assure reproducible fabrication of several tens of thousand units. The three phase contact problem, gaseous (the reacting fluids), liquid (the electrolyte) and solid (the electrodes), has in the beginning of our work brought us to follow the method used very generally at the time, which consists of using porous metals and looking for their best operating conditions. Because, on the one hand, of the disadvantages that we have observed in the utilization of a relatively thick layer, the accumulation in the pores either of products of combustion or nitrogen from the air, and on the other hand of the knowledge of the good diffusion at high temperature of gases through certain metals, we tried the use of these metals in thin compact sheets.

The diffusion of hydrogen through palladium and platinum is a phenomenon which has been known for a long time; further the systematic studies that we have made in this field have shown that the oxidant made of air to which carbon dioxide has been added passes sufficiently rapidly through thin silver sheets to give results at least as good as with the porous substances.

2.1_1 The Anode

In spite of above mentioned advantages, the utilization of palladium in a sheet cannot be considered for economical reasons, because it prohibits the use of any other fuel gas than hydrogen. For these reasons, the anode in our cells is always a graphite cylinder very lightly covered on the surface with palladium (close to 0.1 mg/cm^2).

Graphite has numerous advantages: good electronic conductance, very low expansion coefficient, relatively good mechanical strength and easy construction. Furthermore, in the reducing environment in which it is situated, it has never shown signs of deterioration.

2.1_2 The Cathode

Silver constitutes at the present state of our knowledge, the only metal usable as a cathode. But used as is and without preliminary precaution, in the presence of molten carbonates, it is subject to permanent corrosion. A systematic study has brought to light three principal aspects of the silver corrosion that can be summarized in the following manner; one of machanical nature due to a degradation of the structure and which favors grain formation; another of a chemical nature which can be defined by a limited dissolution in the electrolyte; finally the third of an electrochemical nature making some silver precipitates appear in the electrolyte, which, because of convection currents and variable potential lines in the functioning cells, can settle at different points between the two electrodes.

However, our observations on the inhibiting role of combining with refractory oxides either in the electrolyte bath or in the cathode itself, have lead us to use a film of these oxides in order to materialize the idea of protecting the silver surface.

The film itself is made in a thin layer (0.1 mm) by flame spraying and offers all the qualities of a sheet.

2.1_3 The Electrolyte

Only electrolytes made of molten salts are usable. Among the different possible solutions, carbonates in a mixture judiciously chosen in relation to the temperature have been employed for CO_2 as one of the reaction products and its presence is favorable in particular to their thermal stability.

2.2 Employment of Materials

To satisfy the conditions preceedingly developed: compactness, facility of assembling, good mechanical resistance, small quantities of materials, easy industrial operation, we have studied in the most comprehensive way the best method of construction based on the following principles:

2.2_1 The Active Substance of the Cell (Fig. 2)

On the anode graphite finger palladium is deposited. A layer of refractory oxide, preferably of magnesia or stabilized alumina is deposited on the anode by flame spraying. This very thin layer, just thick enough to assure a good electric insulation contains the carbonates and thus serves as a support for the electrolyte. A silver-based thin film (0.1 to 0.2 mm) which constitutes the cathode is then deposited on the assembly. This metallic film is too thin to insure by itself a sufficient means for current removal and this is achieved by a silver wire fixed along the electrode which can be joined in a battery, to a central conductor.

2.2_2 The Top of the Cell (Figure 3)

The open extremity of the graphite finger is fixed in a brass piece which contains: an axial nozzle that penetrates to the bottom of the anode, its role is to feed fuel to the cell and to collect the anodic current; a radial nozzle through which the excess fuel that has not reacted carries away the products of the reaction water vapor and carbon dioxide.

This part of the cell, is connected to the wall of the exterior enclosure and is maintained at a lower temperature than that of the melting point of carbonates; they solidify and the creepage phenomena that would provoke their disappearance is prevented.

3. CONSTRUCTION OF A LABORATORY BATTERY USING SEMI-INDUSTRIAL ELEMENTS

The experimentation with single cells of various dimensions and method of construction proceeds in different directions with two goals; first to increase electrical performances, and second to prolong their life.

The present conception of the cells would allow a unit of dimensions which are already substantial and the battery that we have made could easily be built on a larger scale. But current densities of the order of 40 mA/cm^2 at 600 mV, and limited longevities, do not permit such an extrapolation.

However, the necessity to come out with a development of gas cells as quickly as possible has lead us to deal with problems created by the grouping of several elements. The latter are many and the following enumeration mentions only the principal ones:

1. Regulation of the unit temperature

2. Effective collection of the current

3. Evacuation and recuperation of the reaction products.

4. Controlled feeding of oxidant and fuel

5. Current Efficiency

6. Starting and stopping of the batteries

7. Analysis of results and evaluation of true efficiency

Accordingly the study and construction of a unit of large laboratory proportions already using some elements at the semi-industrial scale, has been undertaken in parallel with research on single cells.

3.1 Description of the Installation

3.1_1 Choice of the Number of Elements

In order to correspond to the hexagonal disposition generally adopted for the bundles of tubes, we have chosen 7 elements of which one is centrally located. It is necessary to place them in an oven that will insure their heating at the start and to compensate for heat losses while in operation.

3.1_2 The Oven (Figures 4 and 5)

It permits heating to 1000°C the volume containing the seven elements and can be placed under an oxidant pressure of a few tenths of a bar. It contains three superposed resistances, the wiring and regulation of which are independent, the lid of the oven is fixed and supports the tubular cells; the oven can be lowered to give access to the electrodes. The lower part can also be taken apart and easily repaired in the case of electrolyte leakage; it is provided, with devices that secure the positioning and support of the cathodes. This oven is also provided with auxiliaries that include:

1. An elevator assembly made of a platform capable of moving vertically which supports the oven.

2. A lifting crane for the block of cells.

3. The regulation of the independent electrical connections to the three heat zones.

3.1_3 Auxiliaries Insuring the Functioning of the Battery

First let us mention the inlet and outlet circuits of the reactants which present a certain complexity since they must insure constant flows, pressures and mixtures (case of the carbonated oxidant). Furthermore, the products of the reaction are collected and accounted for.

The problem resulting from the utilization of a current produced at several tens of amperes under some hundreds of millivolts has been solved through the use of a rotating device.

The oven is surrounded by a platform of dimensions large enough to allow the technicians to work directly on the tops of the cells: all the controlling and measuring instruments are grouped at this level.

Figure 6 shows a general view of the system, it shows:

1. In the foreground the platform.

2. At the left, the oven.

3. At the right the instruments for measuring, controlling and fuel supply assembled on the same board.

3.1$_4$ Measuring Instruments

The gas reactants are supplied via classical laboratory flow meters, the water produced is retained by collectors followed by weighings: the carbon dioxide is sampled by a mass spectrometer (Fig. 7).

The overall electrical characteristics of the battery and those of each single cell are recorded continuously in order to obtain the most information from each experiment.

To account for results and to calculate the electrical and electrochemical performances of the installation, suitable meters are employed. Let us add that these measurements are completed by taking temperature at numerous points in the installation and inside each cell.

3.2 <u>Experimental Results</u>

The assembling of the complete installation has just been completed but its auxilliary apparatus for production of reformed gas that is intended for use with it, is not yet functioning. This installation has been in operation for too short a time to make it possible to publish definite results that ought to be further substantiated. As an example we shall give the results obtained during the first experiment with a set of 7 cells made under identical but not optimum industrial conditions.

3.2$_1$ Characteristics of a Single Cell

Total Length, mm	Diam., mm	Active Surface, cm^2	Weight, gm/cm^2			
			Cathode	Anode	Electrolyte	Refractory Oxide
800	18	220	0.130	graphite 0.55 palladium 0.002	0.048	0.170

3.2$_2$ Operating conditions

Oxidant air + CO_2 (30%); flow, 300 l/h under 150 m bars. The flow of air is relatively important due to the oversized dimensions of the oven. Fuel industrial hydrogen flow, 50 l/h under 130 m bars. In this experiment the hydrogen is not recycled after use. Temperature of operation: 600°C.

3.2₃ Principal results obtained

This experiment was particularly aimed at determining the efficiency of series and parallel assemblies and in both cases the current potential curves shown on Figures 8 and 9.

The performances obtained with these cells made under poor conditions and for a relatively low test temperature are modest: 20A at 0.5v, which corresponds to a maximum power of 10w.

The duration of the experiment which was limited to approximately ten hours cannot be taken into consideration.

This experiment has shown, however, that the whole installation can satisfy all the technological objectives that we had defined. Furthermore, it will be possible to have twenty cells operate within the same dimensions and the same connections and the usable surface of each one of the cells may be further increased.

4. CONCLUSIONS

The conception of an elementary cell of semi-industrial dimensions which we have reached could, from the technological point of view, lead in the future, without major difficulty, to the construction of a pilot unit. Numerous problems for assembling and handling of materials were solved. They permit the construction of a battery which offers the possibility of studying the behavior of cells fabricated under various conditions, following operating methods apt to be used in industry.

Important progress has been made to considerably reduce the causes of corrosion (some silver cathodes preserved through combination with a coat of refractory oxide have shown no detectable sign of corrosion after operating for a few hundred hours). It is now necessary to ensure an industrial application that we consider, the construction of cells whose lifetime exceeds a year.

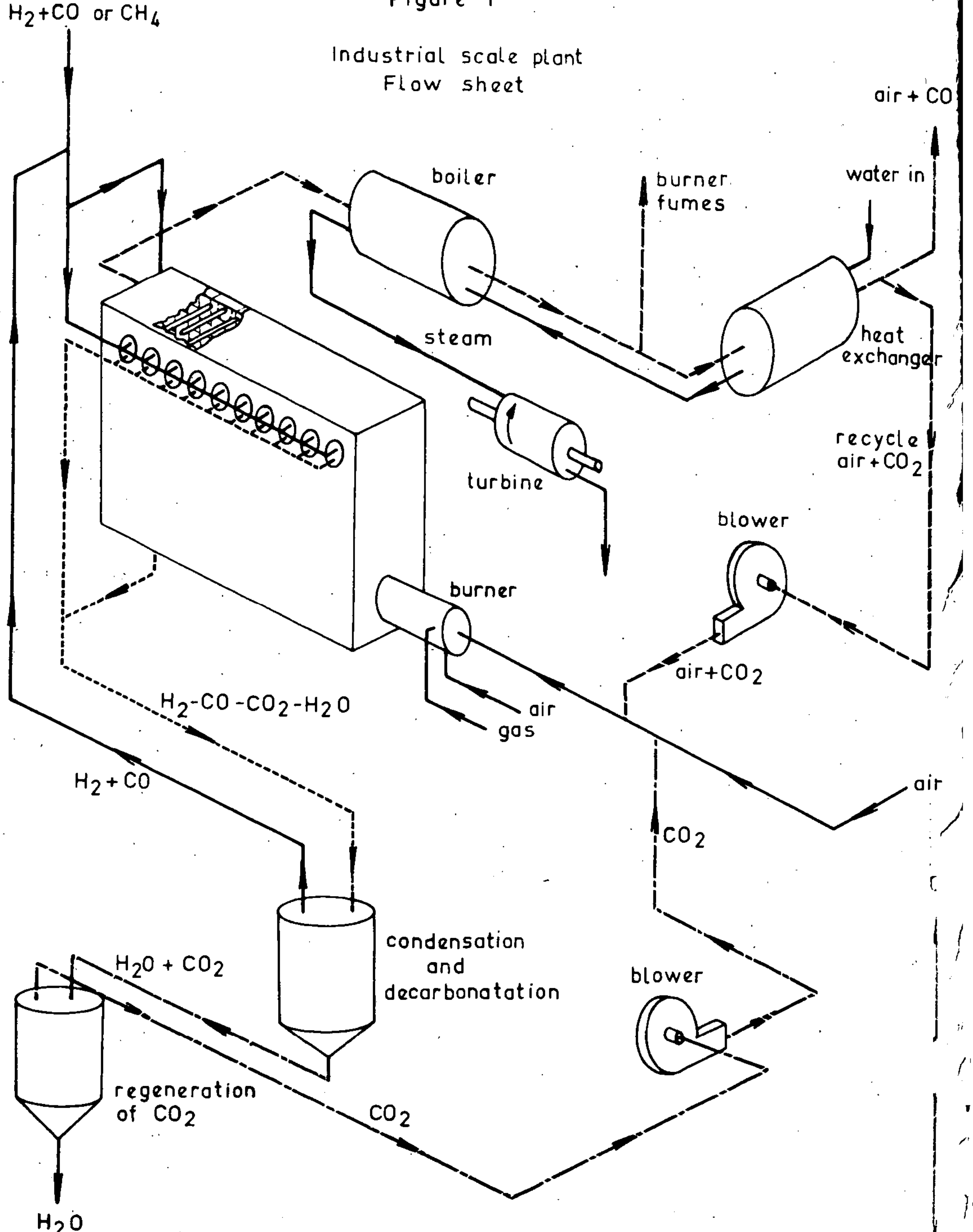
The current densities of some tens MA/cm^2 that we obtained from single cells are insufficient to make a powerful generator operate under advantageous conditions and compete with standard methods of power generation. We do not believe that this problem is impossible to solve in a reasonable period of time because it is difficult to imagine performance of high temperature cells being inferior to those of cold cells.

On the other hand the lifetime of gas cells which depends in particular, on many phenomena of corrosion, on the modification and the change with time of the properties of materials at various temperature, will require important efforts if the research is to be brought to the proper value.

For this purpose, Gaz de France is working in collaboration with specialized laboratories at universities or in industry and particularly with the Compagnie Generale d' Electricité. Gaz de France has obtained a research contract as a result of action of the committee for conversion of energy which is part of the General Delegation for Technical and Scientific Research.

Figure 1

Industrial scale plant
Flow sheet



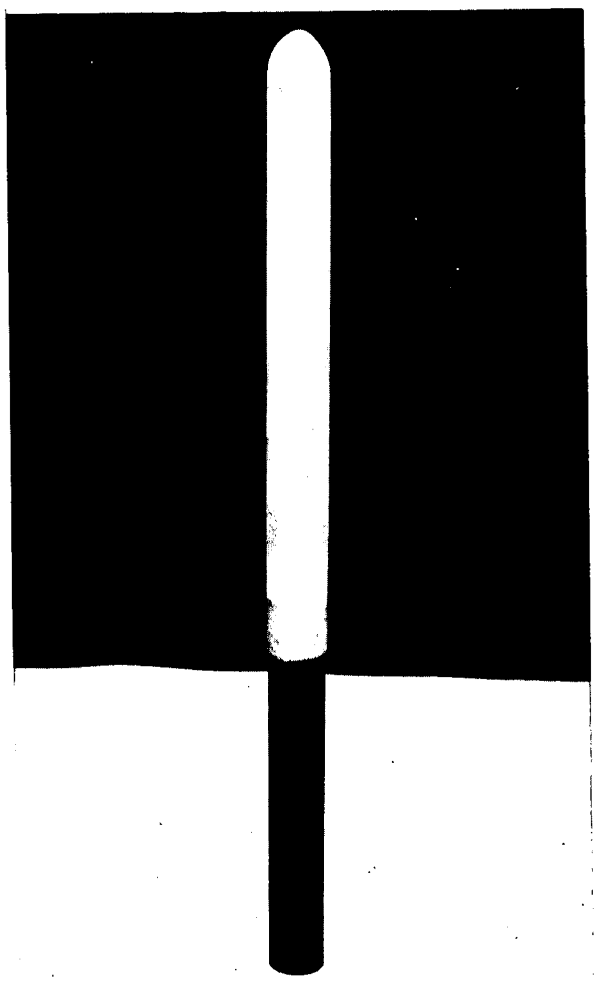


Figure 2: Main Section of a Single Cell

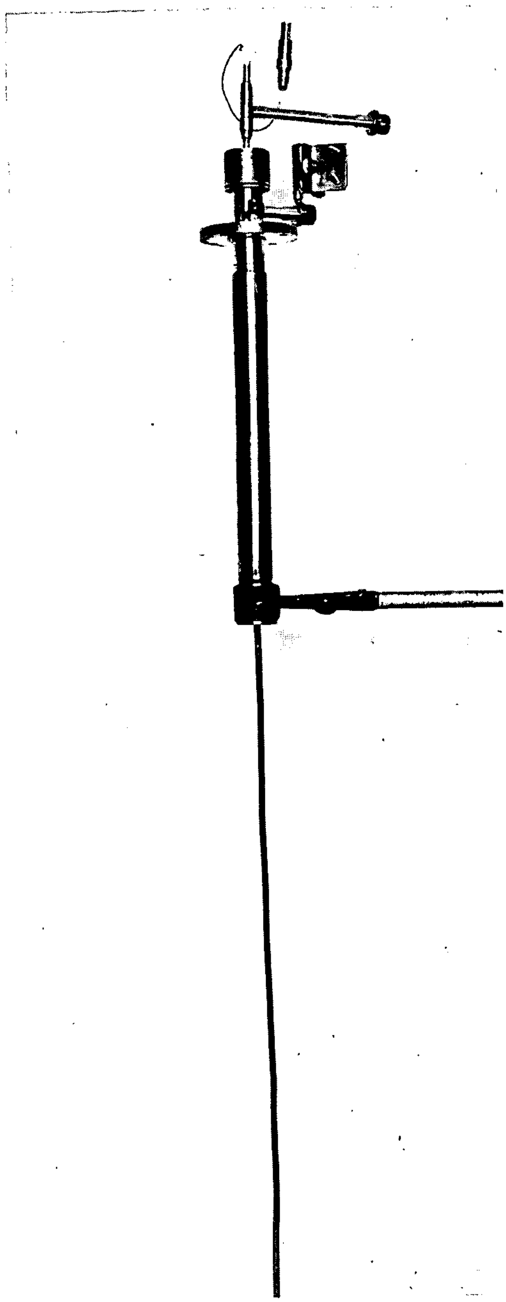


Figure 3: Top of a Single Cell

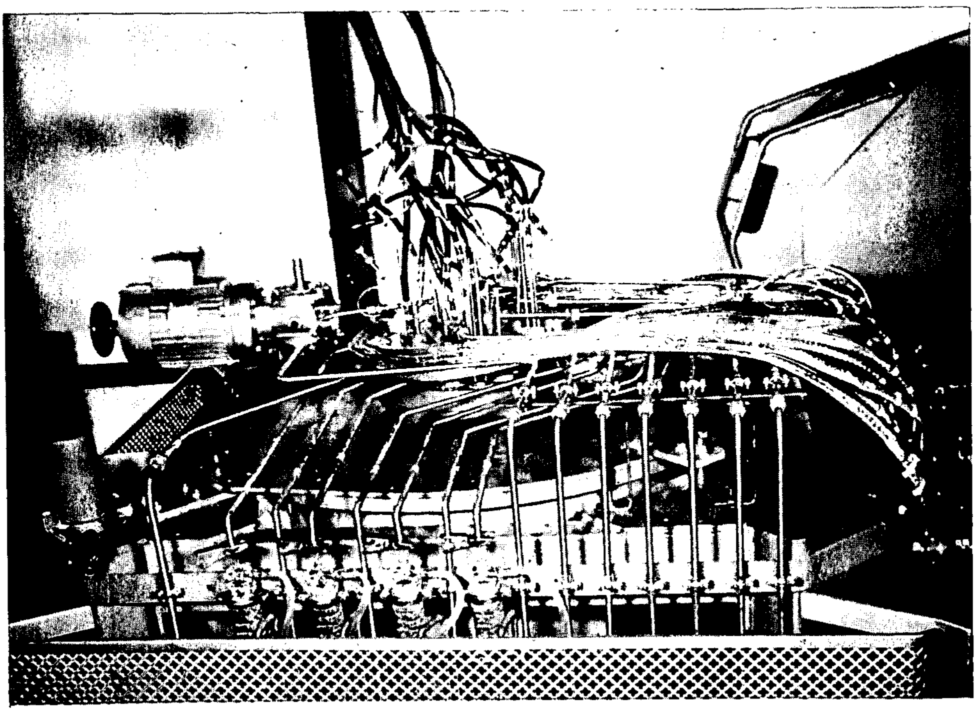


Figure 4: Seven-Element Battery, Top View

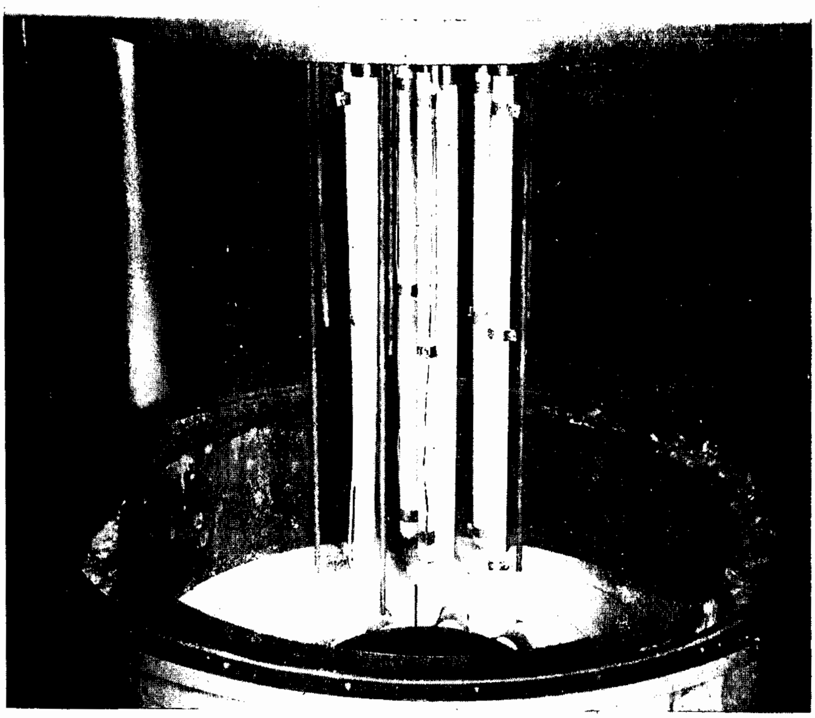


Figure 5: Seven-Element Battery, Bottom View

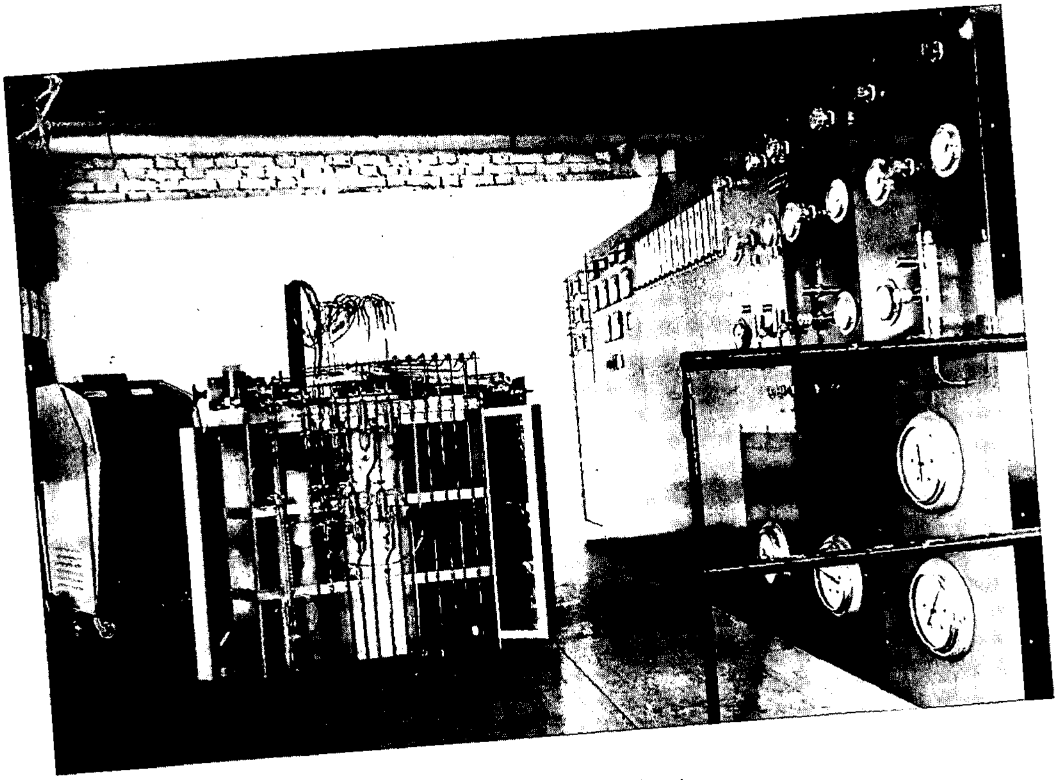


Figure 6: Total System

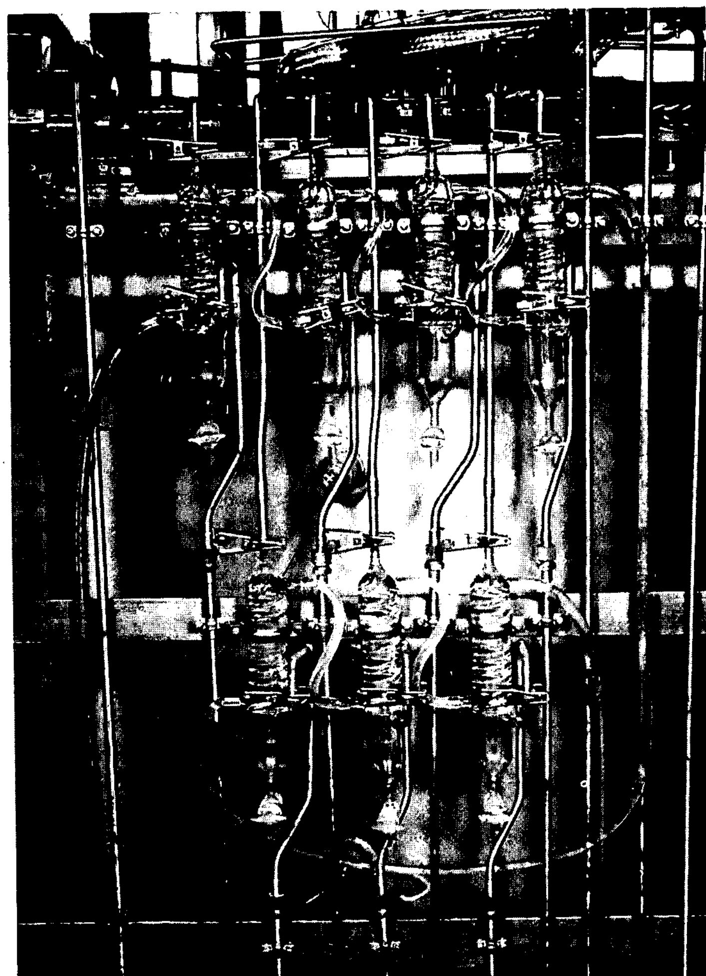


Figure 7: Recovery of the Reaction Products

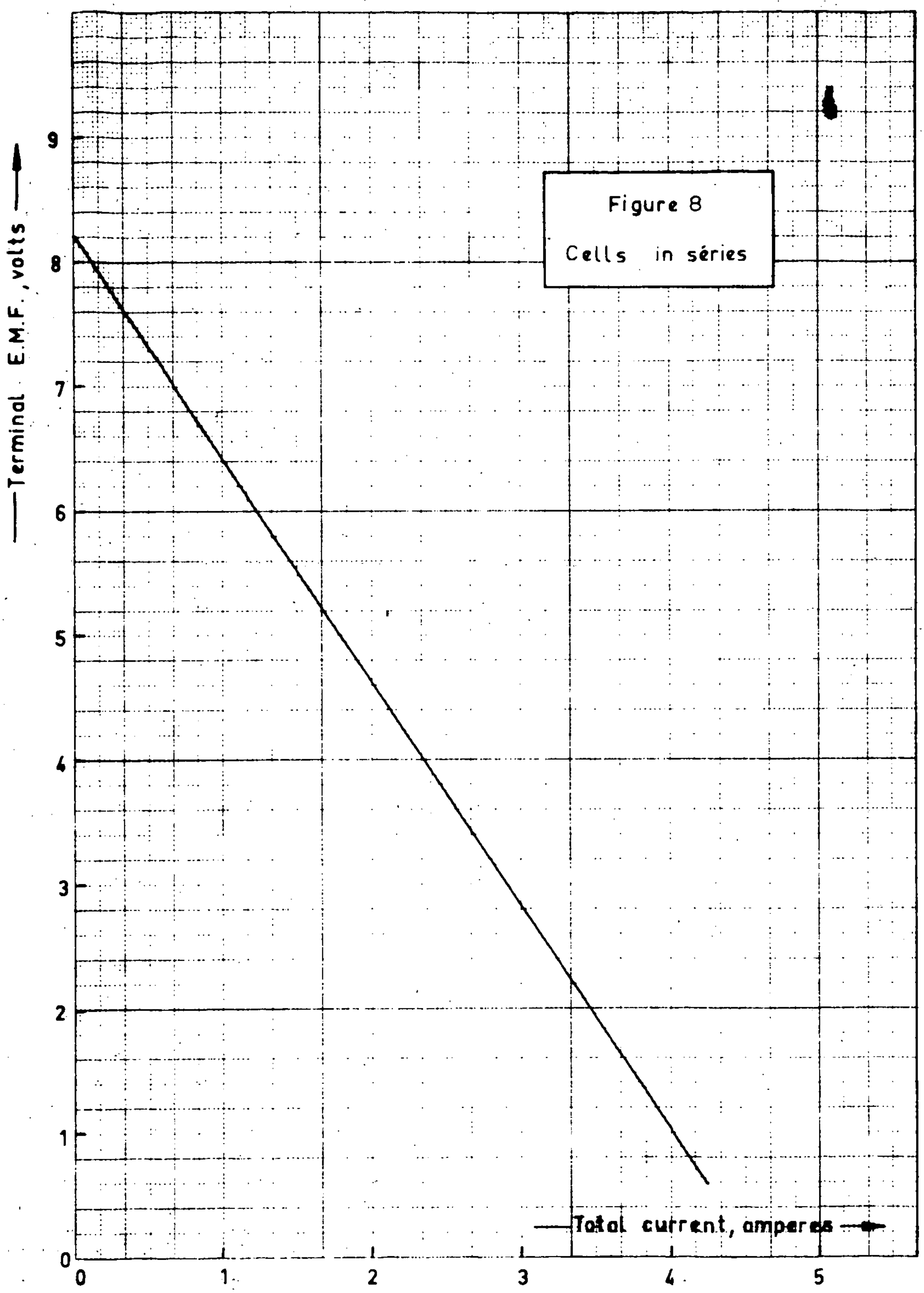


Figure 8
Cells in séries
Terminal E.M.F., volts
Total current, amperes
0
1
2
3
4
5
6
7
8
9
0
1
2
3
4
5

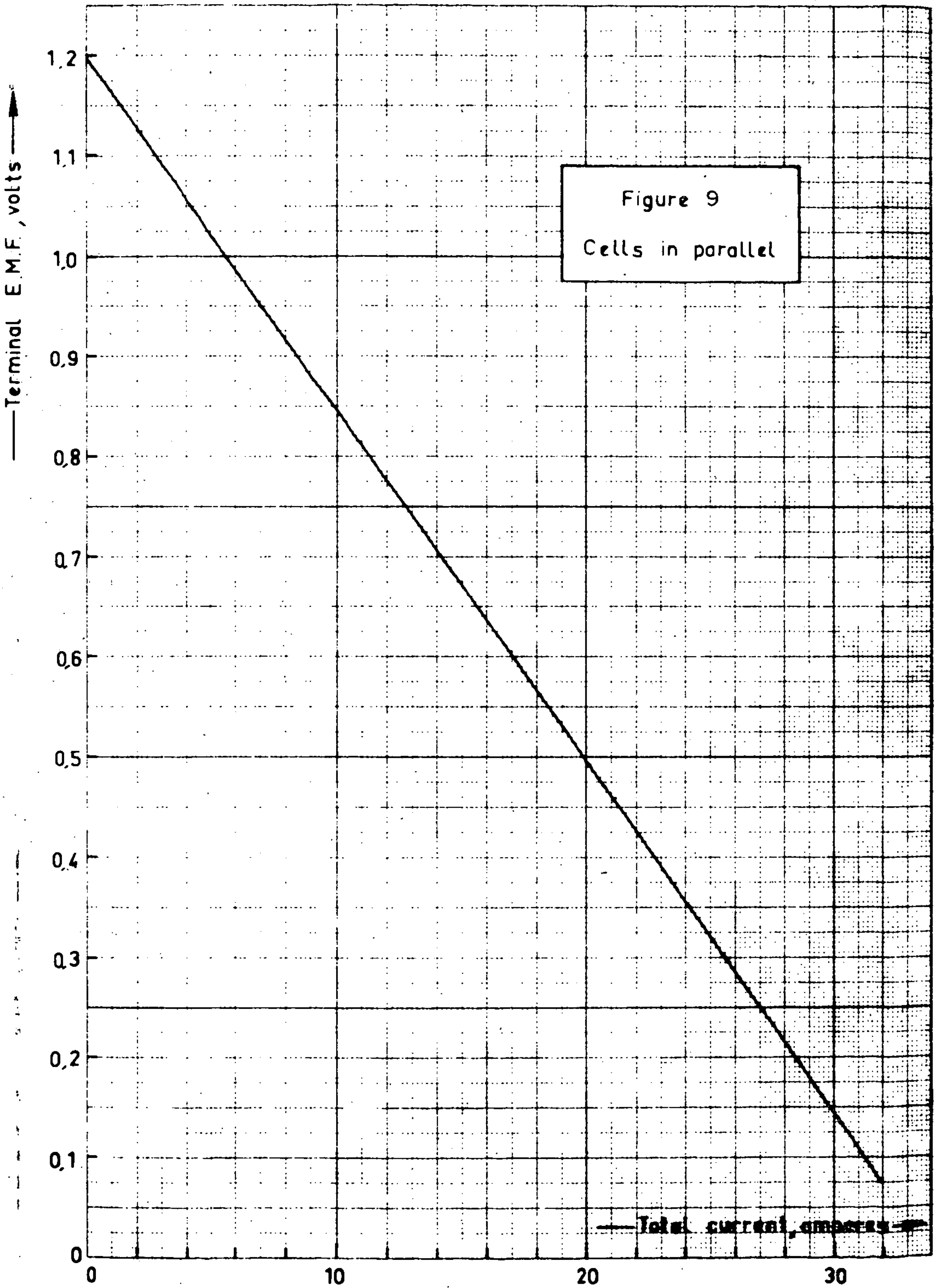


Figure 9
Cells in parallel
Terminal E.M.F., volts
Total current, amperes
1,2
1,1
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
0
10
20
30